

5 Experimental

5.1 Standard operating procedure

All operations were carried out under an inert atmosphere of nitrogen or argon gas using standard Schlenk techniques. Solvents were dried and distilled under an atmosphere of nitrogen. Diethyl ether, hexane and THF were distilled from sodium metal, with benzophenone as indicator for the ethereal solvents. Dichloromethane was distilled from phosphorous pentoxide. Most chemicals were used without prior purification, unless stated otherwise. Column chromatography, using Kieselgel 60 (particle size 0.0063 - 0.200mm) or neutral aluminium oxide 90 was used as resin for all separations.

5.2 Characterization techniques

5.2.1 Nuclear magnetic resonance spectroscopy

NMR spectra were recorded on a Bruker ARX-300 spectrometer and on an AVANCE 500 spectrometer with the help of Mr E.R. Palmer at the University of Pretoria. ^1H NMR spectra were recorded at 300.135 and 500.139 MHz and ^{13}C NMR spectra at 75.469 and 125.75 MHz respectively. The signal of the deuterated solvent was used as reference: ^1H CDCl_3 7.24 ppm, benzene- d_6

7.15 ppm and ^{13}C CDCl_3 77.00 ppm, benzene- d_6 128.00 ppm. For resolution enhancement of the manganese and rhenium complexes, longer acquisition times were achieved by manual shimming and manipulation of the sweep width.

5.2.2 Infrared spectroscopy

Solution IR spectra were recorded on a Perkin-Elmer Spectrum RXI FT-IR spectrophotometer with a NaCl cell. All spectra were recorded using either dichloromethane or hexane as solvent. The vibrational stretching bands in the carbonyl region (ca. 1500 - 2200 cm^{-1}) were recorded for all complexes.

Solid state Fourier Transform infrared (FTIR) spectra were obtained under vacuum as a 1% w/w CsI disk using a Bruker IFS 113 spectrometer over the region 125 – 4000 cm^{-1} with a spectral resolution of 4 cm^{-1} . OPUS 5.5 software was used for data processing.

5.2.3 Raman spectroscopy

Experimental solid-state Raman spectra were obtained with the help of Dr W. Barnard (University of Pretoria) using a dispersive Raman spectrometer. All dispersive spectra were obtained by exciting the samples with the 647.1 nm (red) line of a Spectraphysics 5012 Krypton-ion laser. For the solid-state spectra, an Olympus confocal microscope with a 50X objective was used to focus the laser light on the sample. The scattered light was dispersed and recorded by means of a Dilor XY multichannel Raman spectrometer equipped with a liquid nitrogen-cooled Wright Generation 1 CCD detector. A Linkam RMS 90 cell was employed to obtain the solid-state Raman spectrum for all the complexes measured at non-ambient conditions of $-196\text{ }^\circ\text{C}$, as degradation of the samples were seen at room temperature. All Raman spectra were obtained from the same samples as used for solid state FTIR; as

CsI pellets, in order for heat dissipation by the CsI matrix. The spectral resolution was 3 cm^{-1} , while laser output power at the source (300 – 500 mW) and integration times (30 – 120 seconds) were varied to obtain the best possible spectra. Three to four spectral accumulations were averaged, and the software used for data processing was Labspec 3.03.

5.2.4 Fast atom bombardment mass spectrometry

FAB-MS spectra were recorded on a VG 70SEQ Mass Spectrometer, with the resolution for FAB = 1000 in a field of 8 kV. Nitrobenzyl alcohol was used as solvent and internal standard. All FAB-MS spectra were recorded at the University of the Witwatersrand.

5.2.5 X-ray crystallography

Data collection and structure determinations were done by Mr D.C. Liles, University of Pretoria. X-ray crystal structure analysis was done from data collected at 20 °C on a Siemens P4 Bruker 1K CCK detector and SMART control software using graphite-monochromated, Mo-K α radiation by means of a combination of ϕ and ω scans. Data were corrected for Lorentz polarization effects and data reduction was performed using SAINT+¹ and the intensities were corrected for absorption using SADABS.¹ The structures were solved by direct methods using SHELXTS¹ and refined by full-matrix least squares using SHELXTL¹ and SHELXL-97.² In the structure refinements all hydrogen atoms were added in calculated positions and treated as riding on the atom to which they are attached. All non-hydrogen atoms (except those refined as rigid groups) were refined with anisotropic displacement parameters, all isotropic displacement parameters for hydrogen atoms were calculated as $X \times U_{eq}$ of

¹ SMART (Version 5.054), SAINT (Version 6.45), SADABS (Version 2.10) and SHELXTS/SHELXTL (Version 6.12). Bruker AXS Inc., Madison, Wisconsin, USA, **2001**.

² SHELXS-97 and SHELXL-97. Sheldrick, GM University of Göttingen, Germany, **1997**.

the atom to which they are attached, $X = 1.5$ for the methyl hydrogens and 1.2 for all other hydrogens. In structures **3**, **12** and **23** some disorder was observed. The parameters for the major orientations were refined freely. The minor orientations were refined as rigid bodies with geometries derived from those of the major orientations. Site occupation factors for the major and minor orientations were refined but constrained to sum to 1.0.

5.2.6 UV/Visible spectroscopy

All the complexes were referenced to benzene and spectra measured in a range of 200.0 - 800.0 nm in a quartz sample cell. A Hewlett-Packard 8452A Diode Array spectrophotometer and a Shimadzu UV-2101 PC UV-Vis scanning spectrophotometer were used.

5.3 Electrochemistry

Electrochemical experiments were conducted under the supervision of Prof D.A. Sweigart, Brown University, USA. Voltammetric experiments were done under a blanket of nitrogen that was saturated with solvent. The electrolyte was 0.10 M Bu_4NPF_6 , which was synthesized by metathesis of Bu_4Br and HPF_6 , recrystallized from dichloromethane/hexane, and dried under vacuum. HPLC grade dichloromethane was the solvent employed in all experiments. Once opened, the solvent was kept under argon and contact with the atmosphere was minimized. Additional purification was not deemed necessary or desirable. Cyclic voltammetry was done with EG&G 173/175/179 potentiostatic instrumentation. The working electrode was a 1 mm diameter platinum disk, and the counter electrode was a platinum wire. The reference was a Metrohm Ag/AgCl electrode filled with dichloromethane/ Bu_4NPF_6 and saturated with LiCl; this was separated from the test solution by a salt bridge containing 0.10 M Bu_4NPF_6 in CH_2Cl_2 .

5.4 Preparation of compounds

5.4.1 Preparation of starting material compounds

5.4.1.1 Triethyl oxonium tetrafluoroborate³

Epichlorohydrin (140.0 g, 119 mL, 1.51 mol) was added dropwise to a solution of sodium-dried ether (500 mL) and freshly distilled boron fluoride etherate (284.0 g, 252 mL, 2.00 mol) at a rate sufficient to maintain vigorous boiling (about 1 hour is needed). The mixture was refluxed and allowed to stand at RT overnight. Supernatant ether was withdrawn from the crystalline mass of triethyloxonium tetrafluoroborate under an inert N₂ atmosphere. Crystals were washed with ether; yield 244 - 272 g (85 - 95%).

5.4.1.2 Chloromercury ferrocene⁴

At room temperature (RT) 4.91 g (15.4 mmol) mercury acetate was mixed with 90 mL methanol and dropped into a solution of 2.80 g (15.05 mmol) ferrocene and 25 mol benzene. The solution was left to stir over night at RT. 0.66 g LiCl (15.6 mmol) was mixed with a 5 mL solution of ethanol and water (1:1) and then dropped into the ferrocene solution. The mixture was stirred for 2 hours at RT and then refluxed for 1 hour at 80 °C. The solvent was removed under reduced pressure and collected for Soxhlet extraction with DCM. The extract was washed with water and dried over MgSO₄. The solution was filtered and dried under reduced pressure to give an orange product, with a yield of 4.38 g (68 %).

³ Meerwein, H. *Org. Synth.* **1966**, *46*, 113.

⁴ Fish, R.W.; Rosenblum, M. *J. Org. Chem.* **1965**, *30*, 1253.

5.4.1.3 Bromoferrocene⁴

0.80 g (4.5 mmol) *N*-bromosuccinimide was dissolved in 70 mL dimethylformamide and added to a solution of 1.48 g (3.5 mmol) chloromercury ferrocene in dimethylformamide. The solution was stirred at 0°C for 3 hours. 150 mL of a 10% sodium sulphate solution was added, and the resulting reaction solution was extracted with diethyl ether. The combined organic extracts were washed with water and dried over magnesium sulphate. The solution was filtered and the solvent removed under reduced pressure. Further purification was done with column chromatography on silica gel with hexane. The yellow product bromoferrocene was collected with a yield of 0.35 g (37.5%).

5.4.1.4 Iodoferrocene⁴

A solution of *N*-iodosuccinimide (1.2 g, 5.1 mmol) in 100 mL dichloromethane was added dropwise to a stirred suspension of chloromercury ferrocene (2.10 g, 5.0 mmol) in dichloromethane at 0°C. After allowing the reaction to continue for 12 hours, 50 mL of an aqueous 10% sodium bisulphite solution was added, followed by an equal volume of a 10% sodium carbonate solution. The organic layer was separated and extracted with dichloromethane, followed by successive washings with 10% sodium carbonate solution and water. After drying over water, the solvent from the combined extracts were removed under vacuum, and column chromatography yielded the product iodoferrocene in 77% (1.20 g).

5.4.1.5 Trisamine tricarbonyl chromium⁵

Chromium hexacarbonyl (3.40 g, 16.4 mmol) was added to a solution of 95 mL ethanol, 5 mL degassed water and KOH (5.90 g, 104.6 mmol) in a

⁵ Rausch, M.D.; Moser, G.A.; Zaiko, E.J.; Lipman, A.L. *J. Organomet. Chem.* **1970**, *23*, 185.

pressure flask. Nitrogen gas was bubbled through the solution for 10 minutes, after which the pressure flask was sealed and heated to 110 °C for 6 hours. The container was then removed from the heat source and allowed to cool in an ice bath. To the bright orange solution was added a degassed solution of concentrated NH₃ (aq) (115 mL, 6.10 mol), and reaction was continued for 2 hours with continuous stirring. Thereafter the solution was filtered and the residue washed with ethanol to remove excess ammonia, and the yellow product [Cr(CO)₃(NH₃)₃] was isolated with a yield of 90 % (2.76 g).

5.4.1.6 η^5 -thiophene chromium tricarbonyl⁶

2.5 g (29.4 mmol) thiophene and freshly distilled Et₂OBF₃ (6.26 g, 44.1 mmol) was added to a solution of [Cr(CO)₃(NH₃)₃] (2.76 g, 14.7 mmol) in 100 mL diethyl ether. The reaction mixture was left overnight, and a dark red suspension formed. 50 mL of degassed water was added to the reaction mixture and the solution was stirred vigorously while being saturated with nitrogen gas. Two layers were then allowed to separate. The top organic layer was removed *via* canula under pressure, and the aqueous phase washed with successive portions of ether. After combining the extracts and the red organic layer, the solvent was removed and column chromatography was used to isolate the orange product, which was recrystallized from dichloromethane and hexane to yield 2.42 g, 74% [Cr(CO)₃(η^5 -thiophene)].

5.4.1.7 η^6 -benzene chromium tricarbonyl⁷

To 55 mL of dibutyl ether was added Cr(CO)₆ (1.76 g, 8 mmol) and excess benzene (~ 30 mmol). The reaction mixture was refluxed overnight, whereafter the solvent was removed under pressure. Column chromatography

⁶ Novi, M.; Guanti, G.; Dell'Erba, C. *J. Heterocycl. Chem.* **1975**, *12*, 1055.

⁷ Fischer, E.O.; Goodwin, H.A.; Kreiter, C.G.; Simmons, H.D.; Sonogashira, K.; Wild, S.B.; *J. Organomet. Chem.* **1968**, *14*, 359.

in benzene/hexane eluent, followed by recrystallization of the yellow product [Cr(CO)₃(η⁶-benzene)] (1.11 g, 65%).

5.4.2 Preparation of organometallic complexes

5.4.2.1 General carbene preparation with direct lithiation of ferrocene in the presence of TMEDA⁸

Synthesis of complexes 1 – 4, 22, 23, 27 and 28

To a solution of ferrocene (1.86 g, 10.0 mmol) in hexane was added a mixture of 1.3 mole eq of 1.5 M *n*-BuLi in hexane (13 mmol, 8.66 mL) and 1.3 mole eq TMEDA (13 mmol, 1.96 mL) in the case of the synthesis of Group VI carbene complexes, and 1.5 mole eq *n*-BuLi (15 mmol, 10 mL) with 1.5 mole eq TMEDA (15 mmol, 2.27 mL) for the Group VII carbene synthesis, at RT under an inert N₂ atmosphere. The reaction mixture was refluxed for two hours, after which the hexane was removed under reduced pressure. The reaction mixture was cooled to -78 °C and redissolved in a minimum of THF, after which the starting material metal carbonyl complex was added (10 mmol). After continuous stirring for 2 hours at low temperature, the reaction mixture was allowed to warm to room temperature, after which the solvent THF was evaporated. Dichloromethane was added at -30 °C and a slight excess (10 -15 mmol) of the oxonium salt Et₃OBF₄ or titanocene dichloride was added. After complete alkylation or metalation, followed by thin layer chromatography, the solution was filtered through a short silica gel filter to remove lithium salts, followed by column chromatography with gradient elution with hexane and dichloromethane. Crystallization was achieved from layered dichloromethane/hexane mixtures. The complexes obtained from this reaction method and their yields, are listed in Table 5.1.

⁸ (a) Fischer, E.O.; Öffhaus, E. *Chem. Ber.* **1969**, *102*, 2449, (b) Fischer, E.O.; Rustemeyer, P. *J. Organomet. Chem.* **1982**, *225*, 265, (c) Schubert, U.; Ackermann, K.; Rustemeyer, P. *J. Organomet. Chem.* **1982**, *231*, 323.

Table 5.1 Carbene complexes synthesized from direct lithiation of ferrocene

Starting material metal carbonyl complex (10 mmol)	Product obtained					
	Complex	Colour	Molar mass (g/mol)	Mass (g)	mmol	Yield (%)
[Cr(CO) ₆] 2.20 g	1	Red	434.14	1.36	3.13	31
	3	Dark red	682.26	3.96	5.80	58
[W(CO) ₆] 3.52 g	2	Red	565.98	1.13	1.99	20
	4	Dark red	945.95	3.99	4.22	42
[Cr(CO) ₆] 2.20 g	5	Red brown	618.61	1.85	2.99	30
	8	Dark brown	802.20	3.08	3.84	38
[Mo(CO) ₆] 2.64 g	7	Brown	662.55	0.68	1.02	10
	10	Dark brown	890.09	3.04	3.41	34
[W(CO) ₆] 3.52 g	9	Purple brown	1065.89	7.19	6.75	68
[MnCp(CO) ₃] 2.04 g	22	Red	418.15	1.57	3.76	38
	23	Red	650.30	2.96	4.55	46
[MnCp(CO) ₃] 2.04 g	24	Red	602.61	1.48	2.45	25
	25	Brown	770.21	4.06	5.27	53
[Re ₂ (CO) ₁₀] 6.52 g	27	Dark brown	1547.14	5.07	3.28	33
	28	Red	1095.54	2.21	2.02	20
[Re ₂ (CO) ₁₀] 6.52 g	29	Light yellow	951.78	0.761	0.80	8
	30	Orange	539.30	0.30	0.55	6
	31	Red	1051.07	2.24	2.13	21
	32	Dark red	1079.08	0.41	0.38	4
	33	Dark brown-red	1667.11	4.47	2.68	27
	34	Pink red	1024.59	0.46	0.45	5

5.4.2.2 General carbene complex preparation with aryl lithiation at low temperatures⁸

Synthesis of complexes 6, 12, 13, and 26

The arene (5 mmol) was stirred while adding *n*-BuLi (5.5 mmol, 1.5 M, 3.66 mL) in 40 mL THF at -20 °C under an inert N₂ atmosphere. Stirring was continued for 2 hours. The binary metal carbonyl complex (5 mmol) was added to the reaction mixture at -78 °C, resulting in a change of the reaction mixture to a darker colour while stirring for 1 hour. Stirring was then continued for an additional 30 min at RT. THF solvent was evaporated under reduced pressure. Et₃OBF₄ (6 mmol, 1.15 g) or TiCp₂Cl₂ (6 mmol, 1.49 g) in dichloromethane was added to the reaction mixture at -30 °C and stirred until reaction completion. LiBF₄ salts were removed by filtering and reaction products were purified via column chromatography using hexane/dichloromethane (4:1) as eluent. Recrystallization of products was done by solvent layering of hexane/dichloromethane (1:1). Actual amounts of arene precursors and yields of complexes obtained are given in Table 5.2.

5.4.2.3 Preparation of mixed heteronuclear carbene complex⁹

Synthesis of complex 11

A mixture of *n*-BuLi (2.2 mmol, 1.5 M, 1.47 mL) and TMEDA (2.2 mmol, 0.33 mL) in hexane was added slowly to a solution of ferrocene (2 mmol, 0.37 g) in hexane under inert conditions, and refluxed for 2 hours. Solvent hexane was evaporated after the reaction mixture was cooled down, and a minimum amount of THF was added to dissolve the dilithiated ferrocene. After cooling the reaction mixture down to -78 °C, 1 mole eq of Cr(CO)₆ was added (2 mmol, 0.44 g) and stirred for 1 hour. The reaction mixture was allowed to warm to -

⁹ Aoki, A.; Fujimura, T.; Nakamura, E. *J. Am. Chem. Soc.* **1992**, *114*, 2985.

30 °C and 1 mole eq of $W(CO)_6$ (2 mmol, 0.70 g) was added, and stirred for a further 30 minutes in the cold. After warming the reaction mixture to room temperature, the THF was removed under reduced pressure, and the dimetal bisacylate redissolved in dichloromethane at -30 °C. Reaction quenching was accomplished by the addition of $TiCp_2Cl_2$ (2.2 mmol, 0.55 g), after which the byproduct lithium salts were removed by filtration. Separation of the heteronuclear complex **11** from homonuclear biscarbene complexes **8** and **9** was achieved by gradient elution column chromatography on silica gel with hexane and dichloromethane, after which **11** was crystallized from a dichloromethane/hexane (1:3) solution to yield the dark brown product **11** (MW = 934.04 g.mol⁻¹) (0.50 mmol, 0.47 g, 25 % yield).

Table 5.2 Carbene complexes synthesized from low temperature lithiation of arenes

Starting material metal carbonyl complex (5 mmol)	Starting material arene (5 mmol)	Product obtained					
		Complex	Colour	Molar mass (g/mol)	Mass (g)	mmol	Yield (%)
$[W(CO)_6]$ 1.76 g	FcBr 1.32 g	6	Dark brown	750.45	2.34	3.12	62
$[Cr(CO)_6]$ 1.10 g	$[Cr(CO)_3(\eta^5-C_4H_3S)]$ 1.10 g	12	Dark red	516.70	0.86	1.67	33
$[Cr(CO)_6]$ 1.10 g	$[Cr(CO)_3(\eta^6-C_6H_6)]$ 1.07 g	13	Dark purple brown	646.72	1.61	2.49	50
$[Re_2(CO)_{10}]$ 3.26 g	Fcl 1.56 g	26	Red	866.61	2.08	2.40	48

5.5 Analytical data

Melting points could not be recorded as complexes decomposed during heating. The elemental analyses done for the carbon and hydrogen atoms of the complexes are listed in Table 5.3. The C and H elemental analyses were performed by the analytical laboratories of ARC·LNR Institute for Soil, Climate and Water. Elemental analysis was not performed for complexes **1 – 4**, **11**, **29**, **32** and **34**.

Table 5.3 Analytical data of synthesized carbene complexes

Complex	Molecular formula	Calculated (%)		Found (%)	
		C	H	C	H
5	CrFeTiC ₂₆ O ₆ H ₁₉ Cl	50.48	3.10	51.10	3.09
6	WFeTiC ₂₆ O ₆ H ₁₉ Cl	41.61	2.55	41.65	2.48
7	MoFeTiC ₂₆ O ₆ H ₁₉ Cl	47.13	2.89	47.88	2.87
8	Cr ₂ FeTiC ₃₂ O ₁₂ H ₁₈	47.91	2.26	48.23	2.30
9	W ₂ FeTiC ₃₂ O ₁₂ H ₁₈	36.06	1.70	36.52	1.72
10	Mo ₂ FeTiC ₃₂ O ₁₂ H ₁₈	43.18	2.04	43.76	2.12
12	CrTiC ₂₀ O ₆ H ₁₃ SCl	46.49	2.54	46.97	2.47
13	Cr ₂ TiC ₂₅ O ₉ H ₁₅ Cl	46.43	2.34	46.97	2.26
22	MnFeC ₂₀ O ₃ H ₁₉	57.45	4.58	57.61	4.34
23	Mn ₂ FeC ₃₀ O ₆ H ₂₈	55.41	4.34	56.02	4.19
24	MnFeTiC ₂₈ O ₃ H ₂₄ Cl	55.81	4.01	56.32	3.99
25	Mn ₂ FeTiC ₃₆ O ₆ H ₂₈	56.14	3.66	56.83	3.57
26	Re ₂ FeC ₂₂ O ₁₀ H ₁₄	30.49	1.63	30.86	1.58
27	Re ₄ FeC ₃₄ O ₂₀ H ₁₈	26.40	1.17	26.34	1.35
28	Re ₂ Fe ₂ C ₃₀ O ₈ H ₂₈ Cl ₂	32.89	2.58	33.23	2.76
30	ReFeC ₁₆ O ₆ H ₉	35.63	1.68	36.22	1.59
31	Re ₂ FeTiC ₃₀ O ₁₀ H ₁₉ Cl	34.28	1.82	34.66	1.79
33	Re ₄ FeTiC ₄₀ O ₂₀ H ₁₈	28.82	1.09	29.20	1.01